Supplementary Information
for

Synthesis and energetic properties of high-nitrogen substituted bishomocubanes

Sohan Lal,[a] Lovely Mallick,[b] SundaramRajkumar,[a,c] Oommen P. Oommen,[a,d] SasidharakurupReshmi,[e] NeerajKumbhakarna,[b]*Arindrajit Chowdhury,[b*] Irishi N. N. Namboothiri[a]

[a] Department of Chemistry, Indian Institute of Technology, Bombay, Mumbai 400076, India. [b] Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai 400076, India, E-mail: neeraj_k@iitb.ac.in, arindra@iitb.ac.in. [c] Present address: School of Chemistry, University of Leeds, Leeds LS2 9JT, UK. [d] Present address: Polymer Chemistry Group, Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, Box 538, SE-75121 Uppsala, Sweden. [e] Polymers and Special Chemicals Group, PCM Entity, Vikram Sarabhai Space Centre (VSSC), Thiruvananthapuram, Kerala 695022, India.

Table of Contents

Table S1. Thermodynamic property data for high-nitrogen containing Bishomocubane in the standard Chemkin format

```
THERMO ALL
   200.000  1000.000  6000.000
DADMBHC          IND 14C  12H  14O   0N   6G   200.000  6000.000 1000.0       1
 3.61224950e+01 5.09210740e-02-1.79840350e-05 2.84680410e-09-1.66893490e-13   2
 8.59382850e+04-1.69194080e+026.84911150e+00 2.61471170e-02 2.66545730e-04    3
-3.93900380e-07 1.66024470e-10 9.39559630e+04 5.62255040e+00                  4
DTetzBHC          IND 14C  12H  12O   0N   8G   200.000  6000.000 1000.0       1
 6.92175300e+01 9.56938840e-02-3.38028790e-05 5.35221010e-09-3.13847010e-13   2
 1.38155400e+05-3.51021480e+02 1.03568280e+01 4.39155450e-02 5.48547730e-04   3
-8.06757430e-07 3.39968880e-10 1.54299080e+05 6.80376690e-01                  4
DPTrizDMBHC      IND 14C  28H  26O   0N   6G   200.000  6000.000 1000.0       1
 6.92175300e+01 9.56938840e-02-3.38028790e-05 5.35221010e-09-3.13847010e-13   2
 1.38155400e+05-3.51021480e+021.03568280e+01 4.39155450e-02 5.48547730e-04    3
-8.06757430e-07 3.39968880e-10 1.54299080e+05 6.80376690e-01                  4
DTetzDMBHC        IND 14C  14H  16O   0N   8G   200.000  6000.000 1000.0       1
 4.41842890e+01 5.99421310e-02-2.12392080e-05 3.36984320e-09-1.97885670e-13   2
 1.23550840e+05-2.16977040e+02 8.69570780e+00 3.69242360e-03 4.15924510e-04   3
-5.86290850e-07 2.43980150e-10 1.33815500e+05 6.17377850e-01                  4
END
```

Table S2. Computational time required for selected molecular structures with job running on 4 processors in parallel(Processor specifications: Intel Xeon E5450 Quad-Core 3.0 GHz)

	Computational time (hours)				
Structure / Species	B3LYP/6-31G(d,p)	B3LYP/6-311G(d,p)	B3LYP/6-31+G(d,p)	B3LYP/6-31++G(d,p)	M062X/6-31+G(d,p)
DTetzDMBHC	0.4	0.8	1.5	2.6	2
DPTrizDMBHC	2.4	4.4	19.8	37	28.3
8	–	–	–	1.3	–
17	–	–	–	134.6	–
18	–	–	–	132.9	–
16	–	–	–	147.5	–

Table S3. Atomic coordinates for the optimized structure of DADMBHC**2**obtained using the B3LYP/6-31++G(d,p) level of theory

No.	Atomic symbol	X	Y	Z
1	C	1.00342300	0.63661400	0.29854000
2	C	0.73826600	-0.93776800	0.32936800
3	C	1.69178000	0.88578800	-1.09096900
4	C	2.13711600	-0.56213300	-1.43033500
5	C	2.24310700	0.45185000	1.26081400
6	H	2.21002600	0.90127100	2.25731600
7	C	3.46069300	0.62609700	0.31256100
8	H	1.03593200	1.34680400	-1.83253600
9	H	4.43925700	0.76900200	0.77539900
10	H	2.57253500	-0.67717900	-2.42676400
11	C	2.15395200	-1.06852400	0.96450600
12	C	3.12595400	-0.81285200	-0.24324000
13	H	2.38197300	-1.86022300	1.68326500
14	H	3.93462200	-1.52123700	-0.43350200
15	C	3.00421400	1.61647300	-0.76087700
16	C	0.90316100	-1.42147600	-1.11531000
17	H	0.04412000	-1.18798100	-1.75282500
18	H	1.10166200	-2.50016600	-1.16739300
19	H	2.85466900	2.62908500	-0.36590100
20	H	3.67759600	1.67784500	-1.62411200
21	C	-0.05015300	1.64784400	0.71086400
22	C	-0.37792900	-1.50558400	1.17642000
23	H	0.43851300	2.61536700	0.89180400
24	H	-0.25472200	-2.59591900	1.24693500
25	H	-0.32902700	-1.10320900	2.19926900
26	H	-0.53817800	1.34725800	1.64623500
27	N	-1.05728000	1.84783700	-0.36348800
28	N	-2.23488000	1.88769100	-0.00707100
29	N	-3.35747000	1.94233000	0.20304300
30	N	-2.65960200	-1.79711900	1.08187500
31	N	-3.61024600	-2.30777200	1.45826100
32	N	-1.70684300	-1.18612800	0.58880000

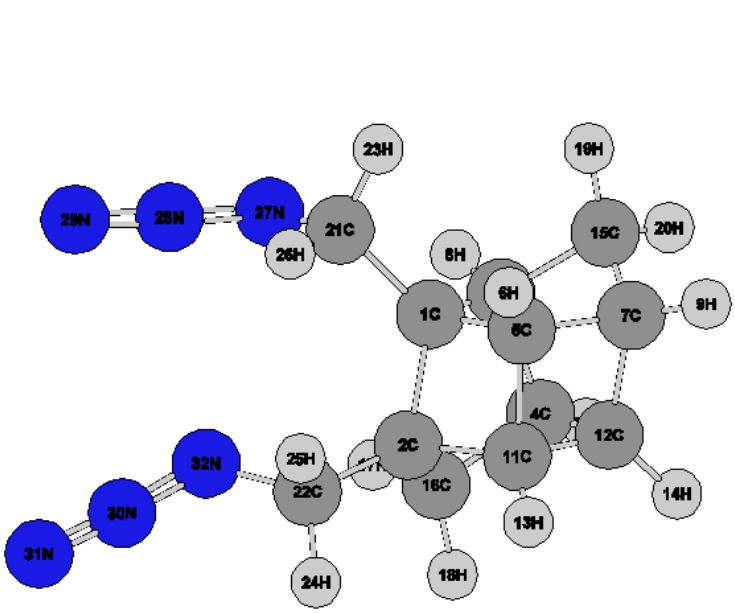
Table S4. Atomic coordinates for optimized structure of DTetzBHC**5** obtained using the B3LYP/6-31++G(d,p) level of theory

No.	Atomic symbol	X	Y	Z
1	C	-0.70051000	0.43137400	-0.04768300
2	C	-0.16474700	-1.06755800	0.24400200
3	C	-1.95671900	0.57557700	0.87734800
4	C	-2.23701200	-0.91978400	1.18145100
5	C	-1.31794900	-0.06986500	-1.41173600
6	H	-0.91156300	0.34013500	-2.33653900
7	C	-2.83752000	-0.12605200	-1.09936900
8	H	-1.79374800	1.20259200	1.75603100
9	H	-3.51717700	-0.21842800	-1.94864400
10	H	-3.04069700	-1.08772100	1.90334100
11	C	-1.09776800	-1.51984900	-0.90974000
12	C	-2.53173700	-1.43300800	-0.26854600
13	H	-0.83173200	-2.36400700	-1.54603500
14	H	-3.19895400	-2.29390300	-0.34259000
15	C	-3.09188900	0.98469300	-0.07717500
16	C	-0.86271700	-1.49779000	1.54138900
17	H	-0.42168300	-1.04975300	2.43766400
18	H	-0.86216500	-2.58897300	1.65362900
19	H	-2.96328100	1.98770000	-0.50133400
20	H	-4.07679900	0.93059500	0.40171500
21	N	1.12338600	1.81432000	-1.08150700
22	N	1.83416800	2.85611900	-0.73201200
23	N	1.86693000	-1.91329000	-0.93277400
24	N	3.14681500	-1.87943600	-0.57668600
25	N	1.38691400	3.20283700	0.46844800
26	N	3.38139500	-1.31254200	0.60054200
27	C	0.25501800	1.56312000	-0.05646200
28	C	1.28872500	-1.31995400	0.11313100
29	N	0.40726100	2.43975500	0.93941700
30	N	2.20887000	-0.95107700	1.05440100
31	H	1.76774400	3.98720300	0.98136100
32	H	3.88883700	-2.24766200	-1.15705700

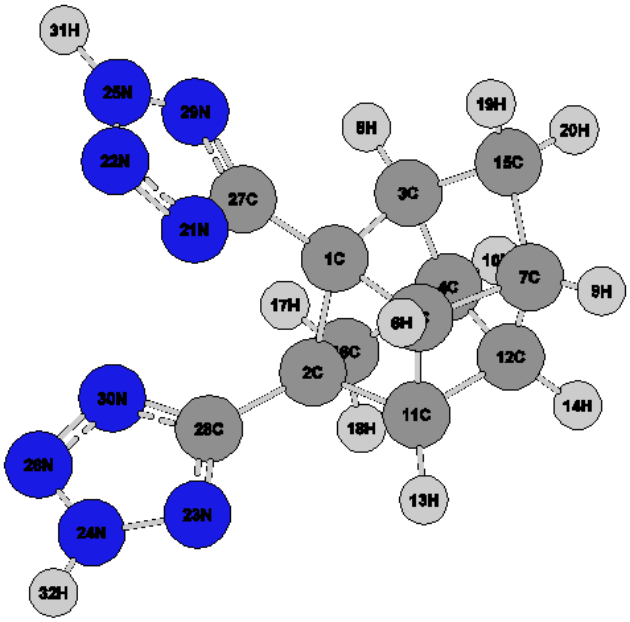
Table S5. Atomic coordinates for optimized structure of DPTrizDMBHC**3** obtained using the B3LYP/6-31++G(d,p) level of theory

No.	Atomic symbol	X	Y	Z
1	C	2.04633700	0.56700600	0.84805500
2	C	1.83777300	-0.87919900	0.17740000
3	C	2.29938300	1.51557200	-0.37972600
4	C	2.66069400	0.47066500	-1.46713500
5	C	3.51849100	0.15564600	1.25456400
6	H	3.76534900	0.08720800	2.31756800
7	C	4.40451500	0.93421200	0.24342500
8	H	1.45791800	2.16132300	-0.63421700
9	H	5.47120500	1.00437200	0.46504300
10	H	2.78425000	0.89275600	-2.46793700
11	C	3.38182500	-1.05257500	0.29789600
12	C	3.95760100	-0.13020500	-0.83408900
13	H	3.82214800	-2.03862800	0.47011300
14	H	4.69036800	-0.53871500	-1.53261300
15	C	3.63335900	2.21636500	-0.07531000
16	C	1.59190600	-0.62175400	-1.31478500
17	H	0.58495000	-0.25500300	-1.54467200
18	H	1.79390600	-1.51196000	-1.92612000
19	H	3.57415200	2.90812800	0.77200000
20	H	4.02278700	2.76175600	-0.94298100
21	C	1.18061500	1.12629700	1.98842000
22	C	1.08303900	-1.99324100	0.88886900
23	H	1.81739900	1.72938100	2.64165500
24	H	1.38297600	-2.95352700	0.45288500
25	H	1.33605000	-2.02586400	1.95207300
26	H	0.74464000	0.32627600	2.59277000
27	N	0.09361600	2.01898500	1.58642200
28	N	0.35318800	3.33667700	1.41062900
29	N	-0.75118800	3.90759600	1.01873100
30	N	-1.07998500	-1.61348900	1.95056000
31	N	-2.34945500	-1.67939300	1.65155200
32	N	-0.37961800	-1.93337500	0.84086400
33	C	-1.20490600	1.74902000	1.30238300
34	C	-1.22100300	-2.22116900	-0.18313700
35	C	-1.74822700	2.97119900	0.93492200
36	C	-2.49404700	-2.05341800	0.34160600
37	C	-3.81352000	-2.22290700	-0.28406500

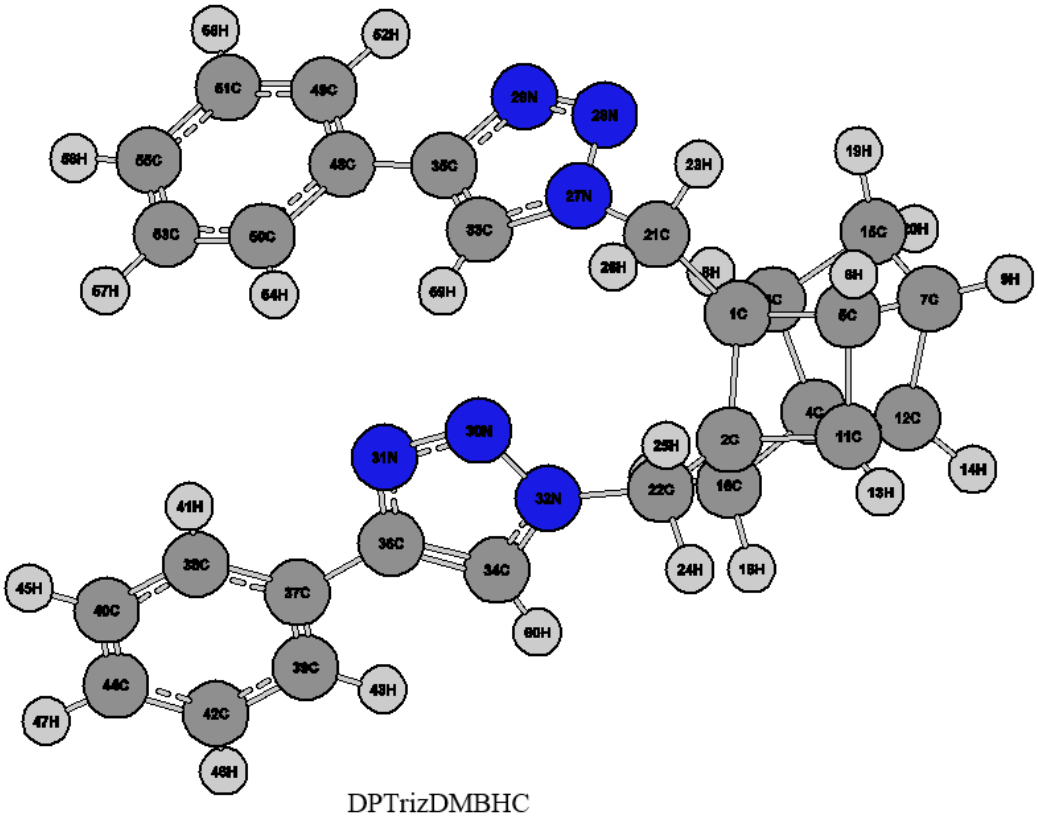
38	C	-4.97417700	-2.20827100	0.50847500
39	C	-3.94402000	-2.40166900	-1.67174400
40	C	-6.23066200	-2.36951200	-0.07577500
41	H	-4.87778100	-2.07160000	1.58023300
42	C	-5.20170000	-2.56581000	-2.25244900
43	H	-3.06187100	-2.40179800	-2.30598500
44	C	-6.35106400	-2.55039100	-1.45694100
45	H	-7.11804700	-2.35712000	0.55059400
46	H	-5.28406100	-2.69937200	-3.32719400
47	H	-7.33018900	-2.67636900	-1.90950600
48	C	-3.11693900	3.31573900	0.52390200
49	C	-3.44969400	4.64882000	0.22729600
50	C	-4.11387000	2.33059900	0.41596300
51	C	-4.74515500	4.98383500	-0.16726500
52	H	-2.68309500	5.41161300	0.31095300
53	C	-5.40854000	2.66952600	0.02182200
54	H	-3.88202600	1.29350300	0.64032100
55	C	-5.73093300	3.99774800	-0.27220200
56	H	-4.98552900	6.01919100	-0.39249500
57	H	-6.16428100	1.89325700	-0.05680900
58	H	-6.73907100	4.26091600	-0.57928900
59	H	-1.62822700	0.76597000	1.42492000
60	H	-0.86348600	-2.52545300	-1.15360800



DADMBHC



DTetzBHC



DPTrizDMBHC

Figure S1. Molecular structures of BHC-based compoundsobtained using the B3LYP/6-31++G(d,p) level of theoryalong with the atom numbering scheme.

Table S6. Comparison of selected bond lengths among high-nitrogen containing bishomocubanes(molecular structures obtained using the B3LYP/6-31++G(d,p) level of theory are shown above for ready reference)

Bond	Bond length (Å)		
	DADMBHC 2	**DTetzBHC 5**	**DPTrizDMBHC 3**
C1–C2	1.5969	1.6183	1.6077
C1–C3	1.5706	1.5667	1.5720
C1–C5	1.5802	1.579	1.5817
C1–C21	1.5174	–	1.5371
C2–C11	1.5571	1.5512	1.5584
C2–C16	1.5324	1.5348	1.5341
C2–C22	1.5119	–	1.5221
C3–C4	1.5524	1.5515	1.5508
C3–C15	1.5380	1.5385	1.5373
C4–C12	1.5652	1.5661	1.5633
C4–C16	1.5363	1.5337	1.5359
C5–C7	1.5531	1.5524	1.5536
C5–C11	1.5515	1.5501	1.5472
C7–C12	1.5785	1.5786	1.5792
C7–C15	1.5302	1.5308	1.5298
C11–C12	1.5712	1.5732	1.5696
$(C_{Methyl}–N_{Azo})_1$	1.4861	–	1.5371
$(C_{Methyl}–N_{Azo})_2$	1.4877	–	1.5221
$(C_{cage}–C_{Tetz})_1$	–	1.4812	–
$(C_{cage}–C_{Tetz})_2$	–	1.4810	–
$(C_{Methyl}–N_{Triz})_1$	–	–	1.4629
$(C_{Methyl}–N_{Triz})_2$	–	–	1.4647

Table S7. Comparison of selected bond angles among high-nitrogen containing bishomocubanes(molecular structures obtained using the B3LYP/6-31++G(d,p) level of theory)

Angle	Value (°)		
	DADMBHC	**DTetzBHC**	**DPTrizDMBHC**
C2–C1–C3	104.2574	104.1397	103.7607
C2–C1–C5	90.1852	89.4921	89.6565
C2–C1C21	122.4452	–	124.313
C3–C1–C5	102.3258	103.0467	101.9959
C3–C1–C21	116.0389	–	116.778
C5–C1–C21	117.2037	–	115.3516
C1–C2–C11	86.5429	86.381	86.5195
C1–C2–C16	105.9706	105.1562	105.9972
C1–C2–C22	120.2444	–	121.8506
C11–C2–C16	105.0821	105.8705	104.6357
C11–C2–C22	114.2773	–	111.9441
C16–C2–C22	119.2802	–	119.8685
C1–C3–C4	99.8554	99.8967	100.2875
C1–C3–C15	105.0406	104.4637	105.0754
C4–C3–C15	104.196	104.1582	104.1134
C3–C4–C12	99.4878	99.6932	99.6905
C3–C4–C16	104.2684	104.3205	104.3336
C12–C4–C16	105.2069	105.2128	105.2932
C1–C5–C7	103.3043	102.7348	103.4861
C1–C5–C11	87.3175	87.8012	87.8203
C7–C5–C11	92.20	92.2936	92.2519
C5–C7–C12	86.9306	86.9191	86.8414
C5–C7–C15	105.489	105.7096	105.5536
C12–C7–C15	106.245	106.3492	106.2665
C2–C11–C5	92.7429	93.0703	92.777
C2–C11–C12	103.6054	103.2391	104.0227
C5–C11–C12	87.2371	87.1849	87.3995
C4–C12–C7	104.774	104.6209	104.5971
C4–C12–C11	102.6042	102.9387	102.3331
C7–C12–C11	90.5082	90.4444	90.448
C3–C15–C7	95.6032	95.6661	95.5442
C2–C16–C4	95.9222	95.9391	95.9881

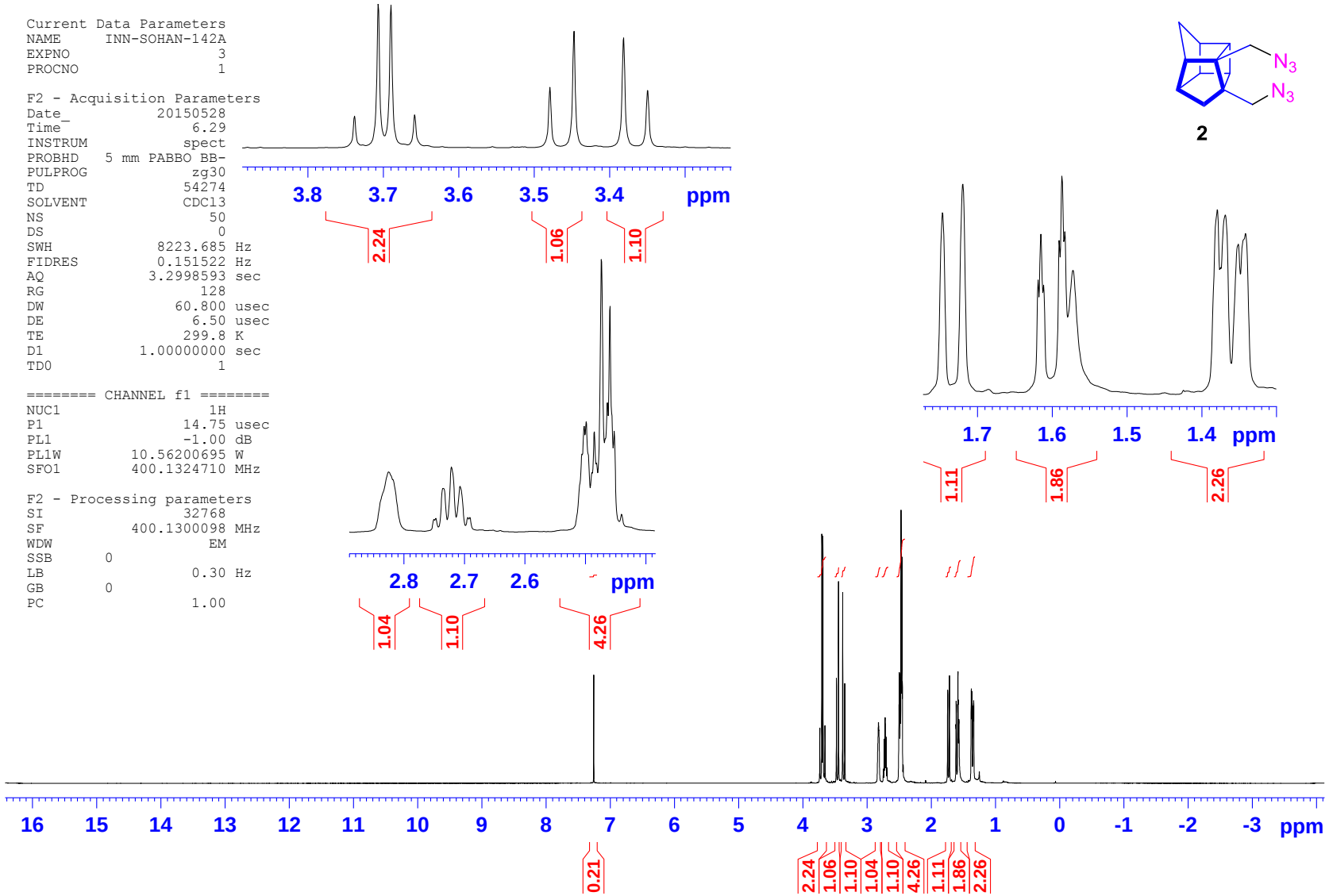


Fig. S2. ^{1}**H NMR Spectrum of DADMBHC 2**

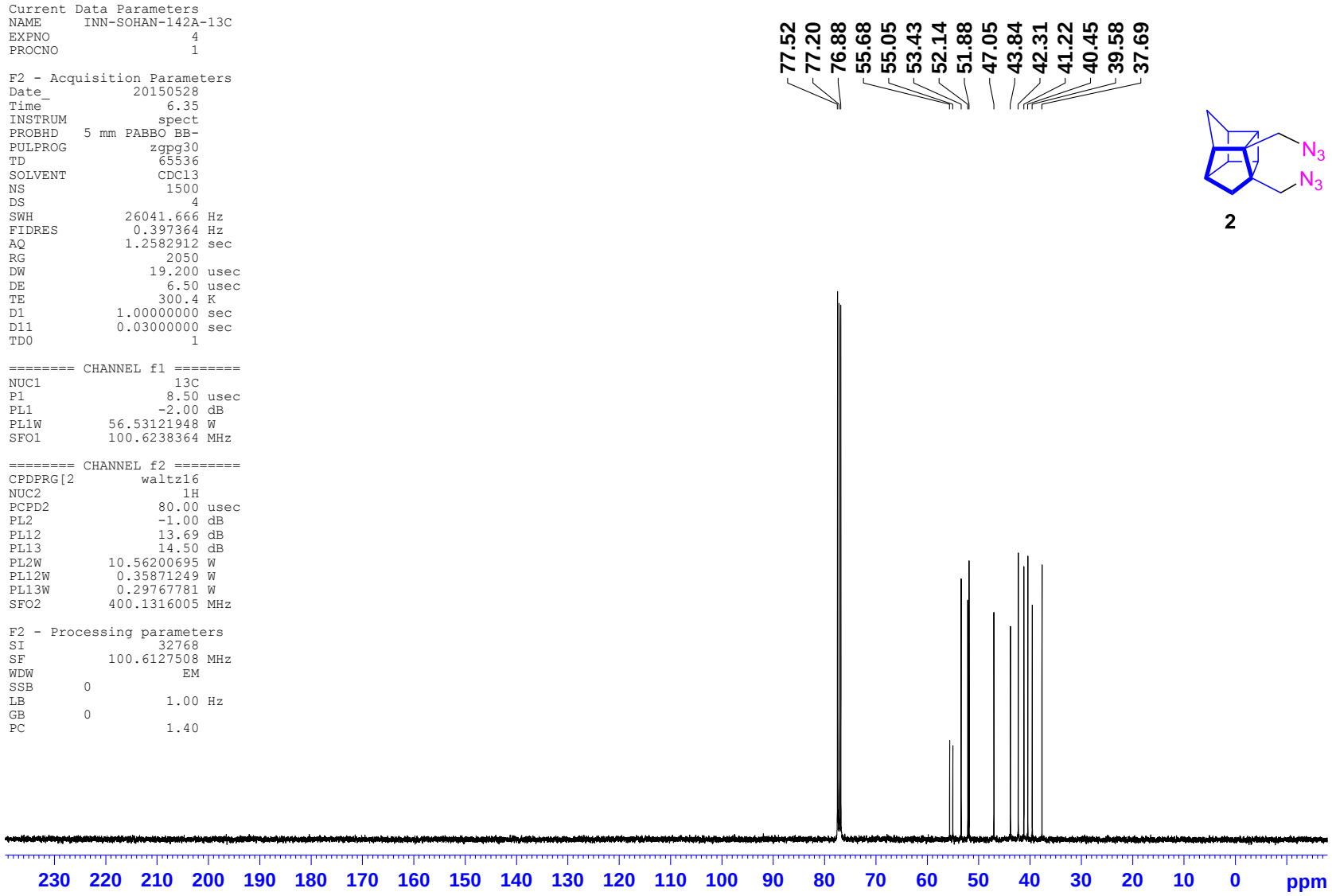


Fig. S3.^{13}C NMR Spectrum of DADMBHC2

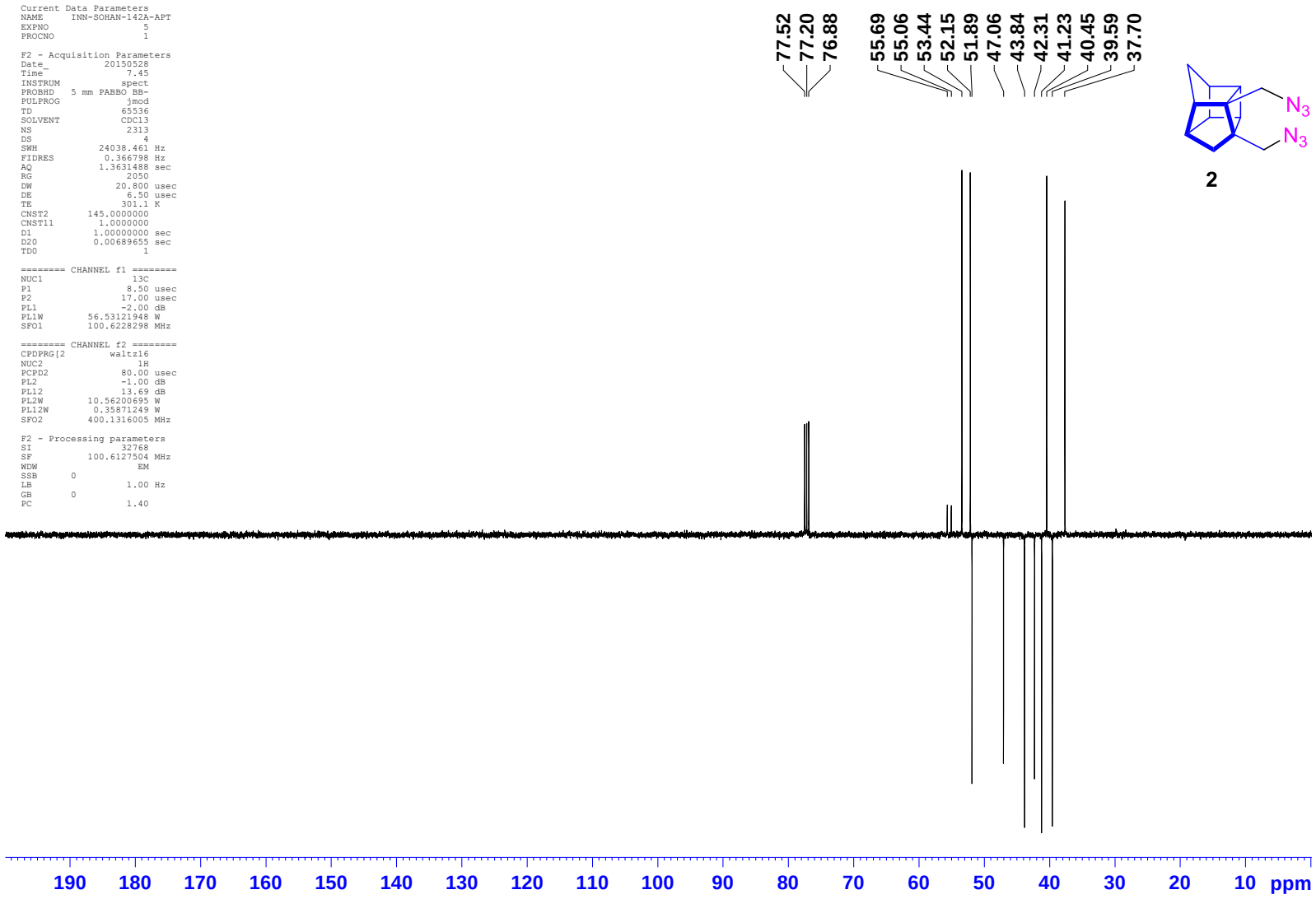


Fig. S4.^{13}C-APT NMR Spectrum of DADMBHC 2

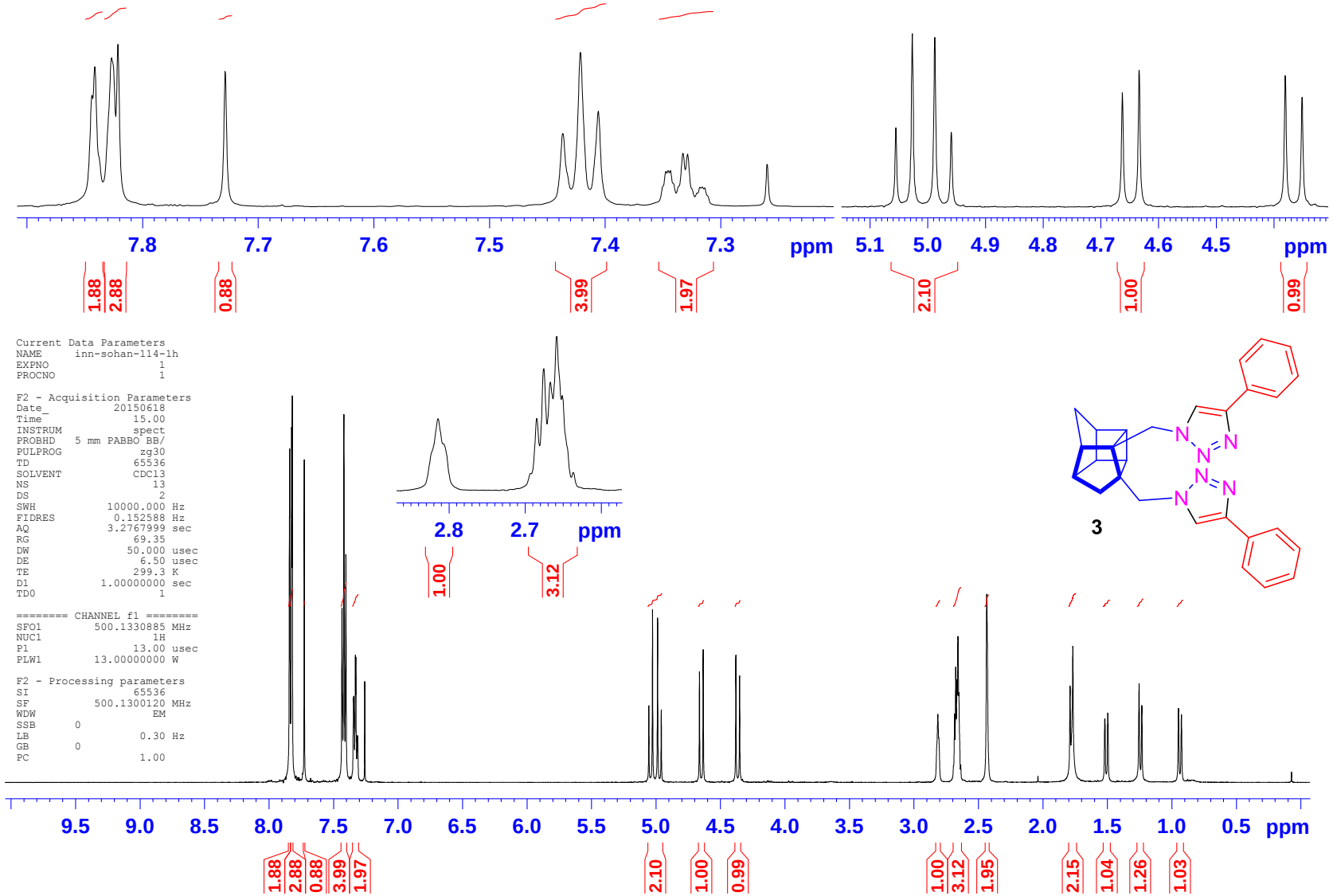


Fig. S5.^{1}H NMR Spectrum of DPTrizDMBHC3

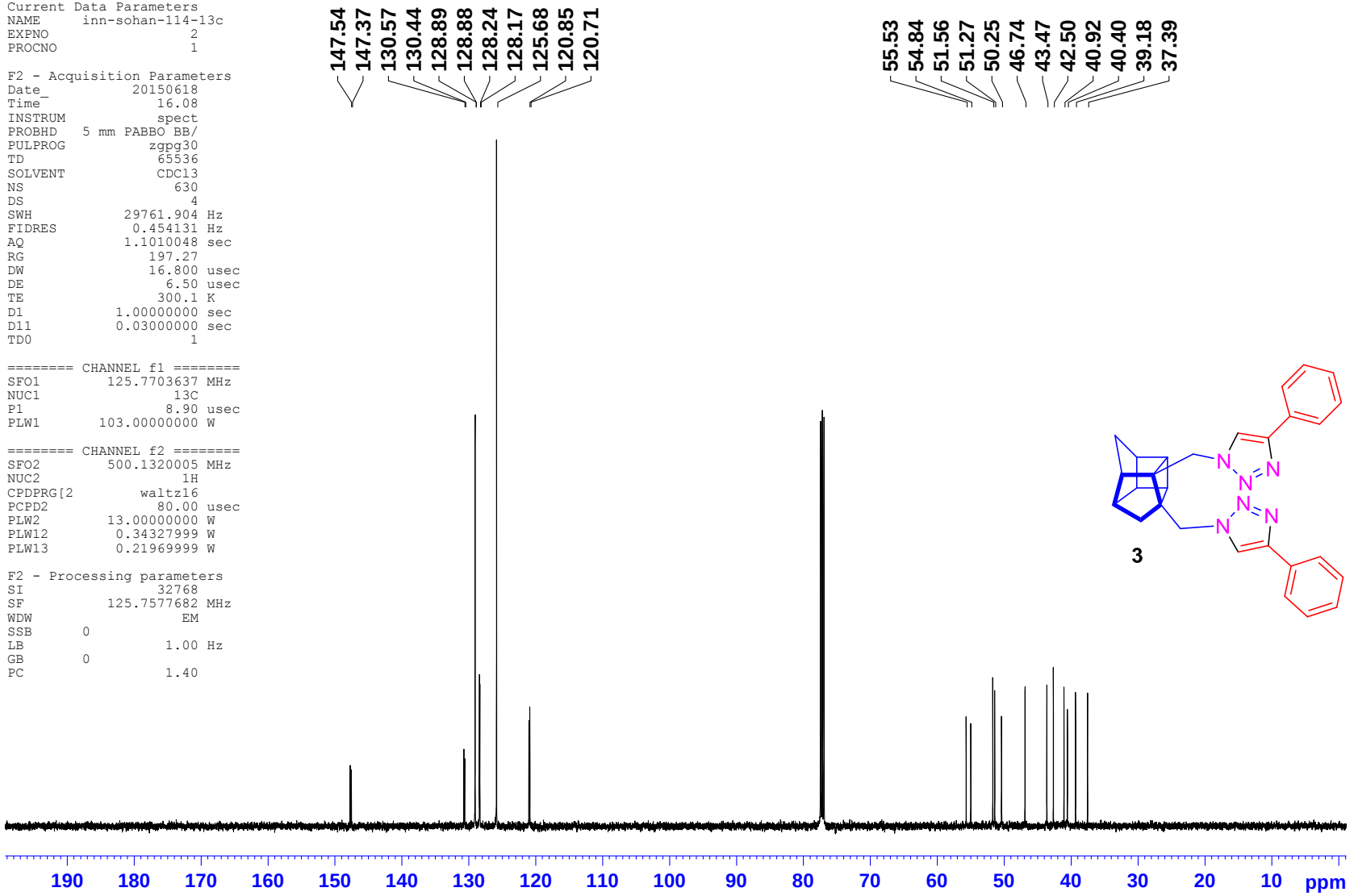


Fig. S6.^{13}C NMR Spectrum of DPTrizDMBHC3

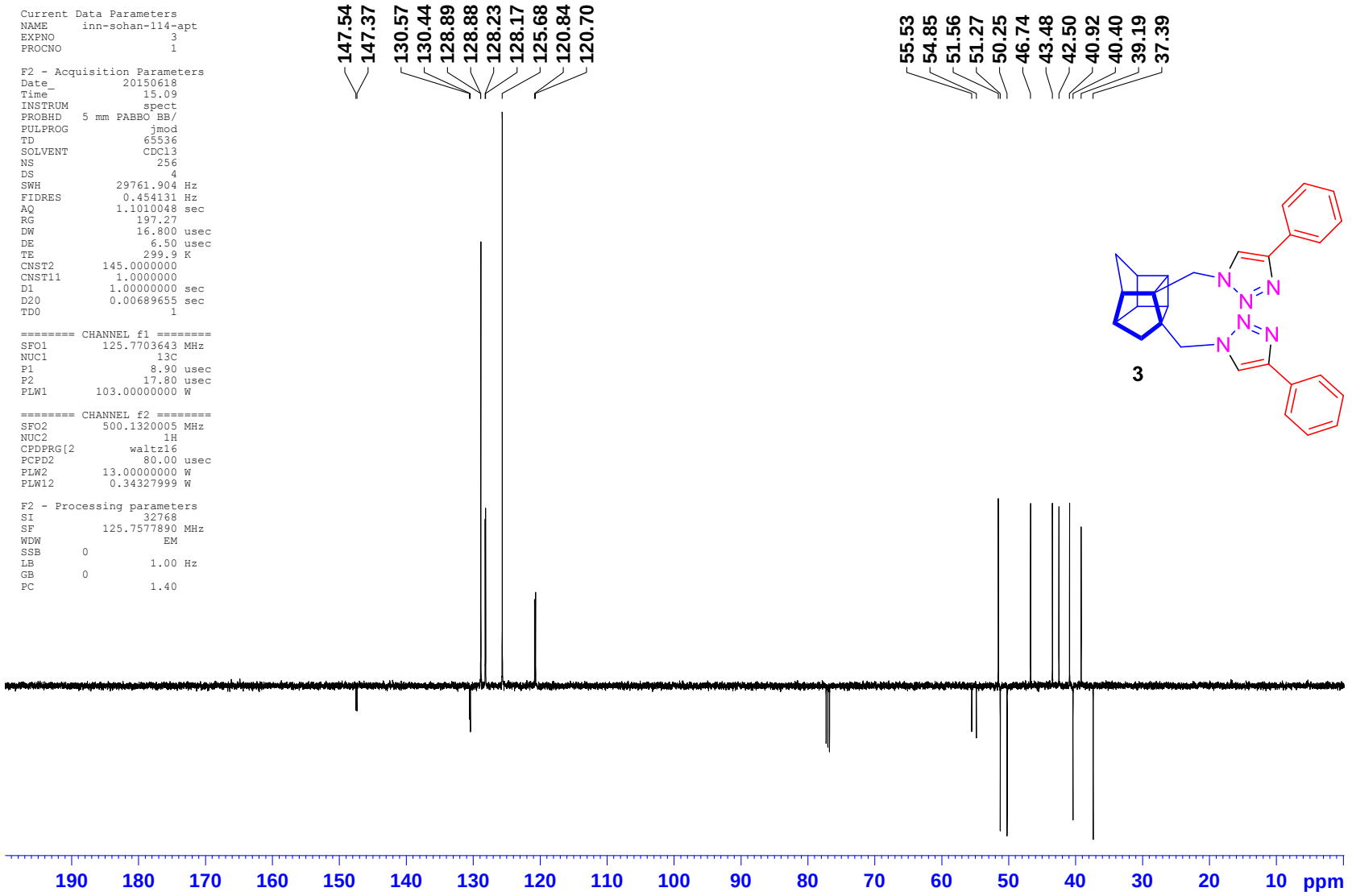


Fig. S7.^{13}C-APT NMR Spectrum of DPTrizDMBHC3

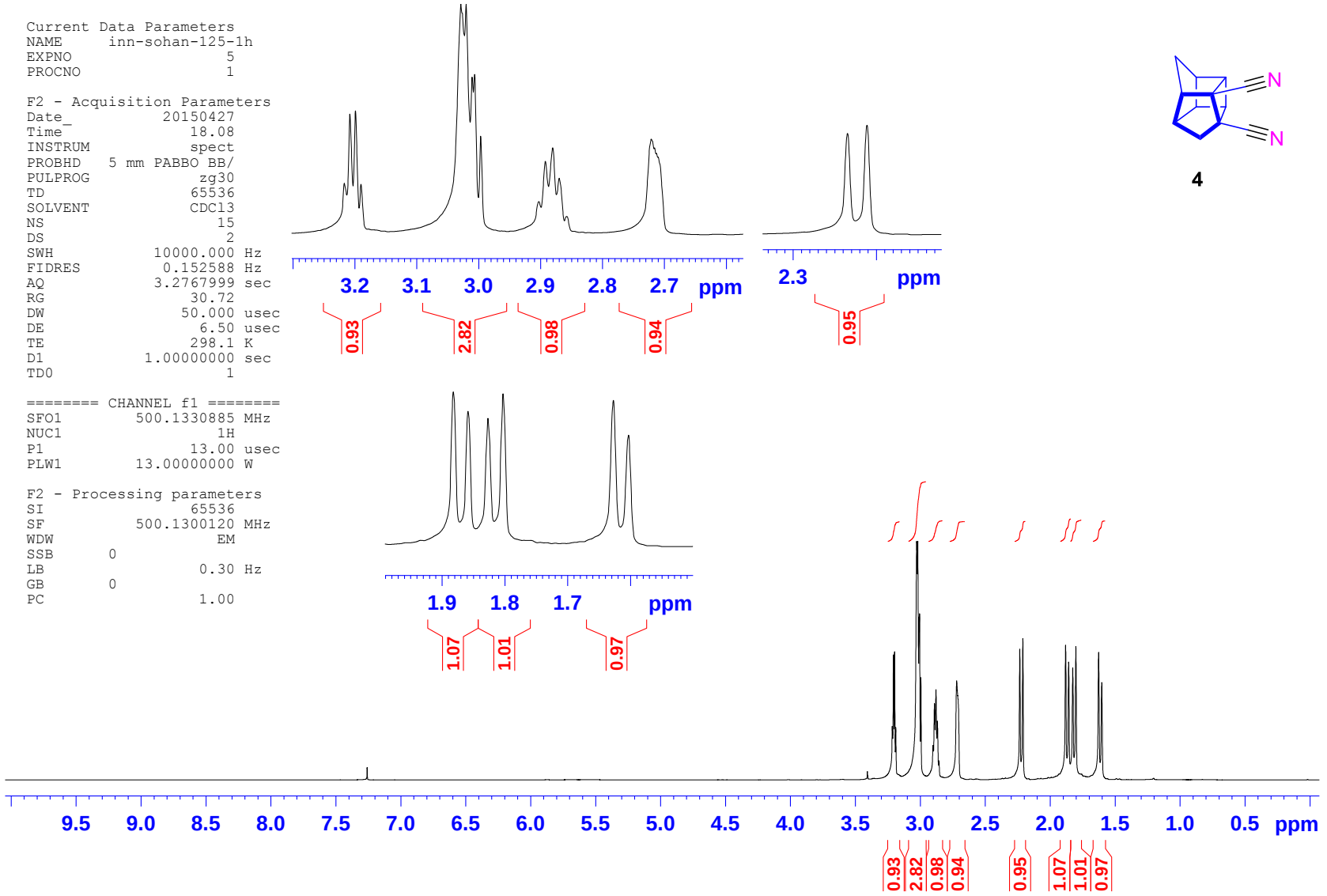


Fig. S8. ^{1}**H NMR Spectrum of DCBHC 4**

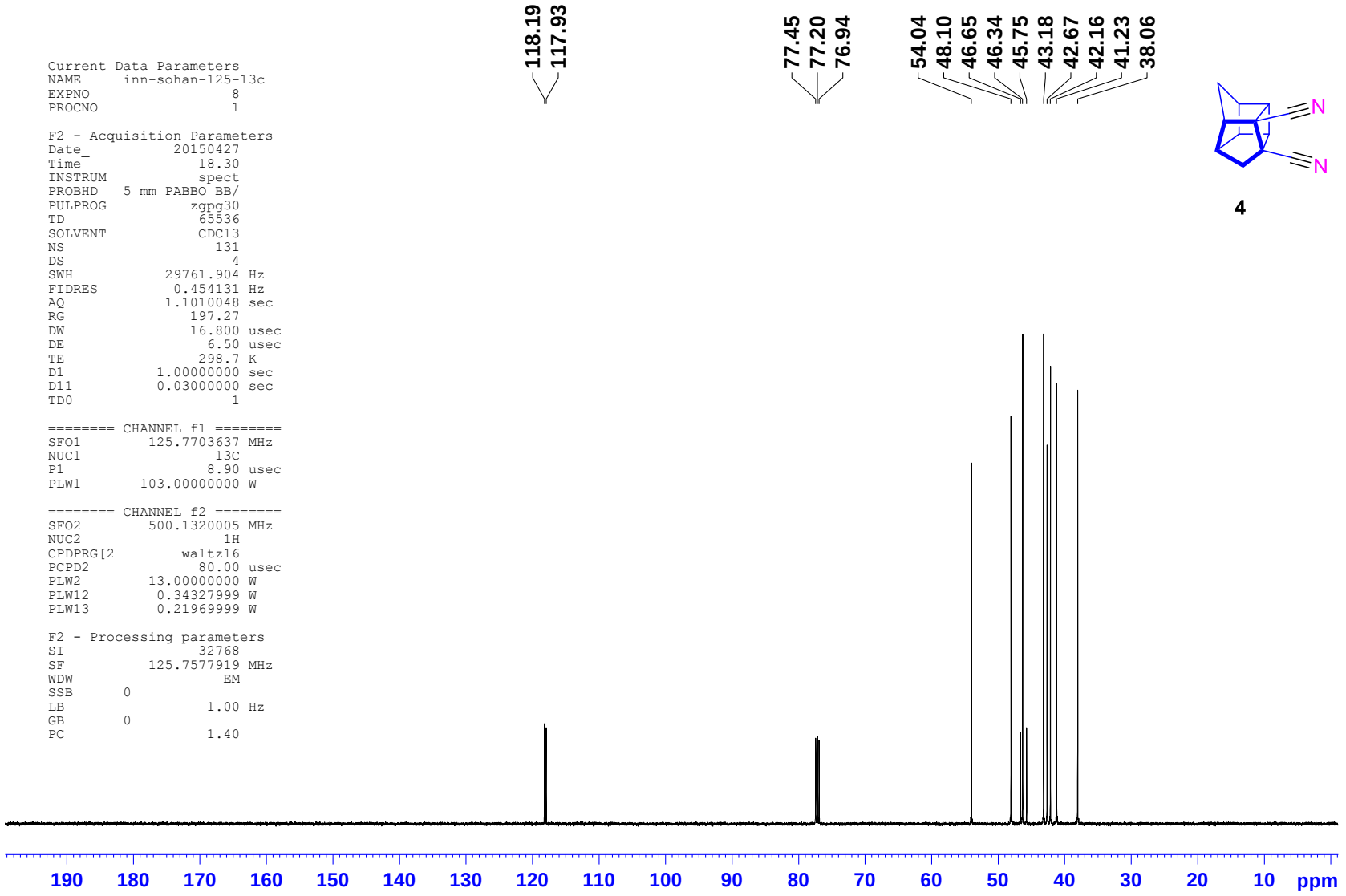


Fig. S9.^{13}C NMR Spectrum of DCBHC 4

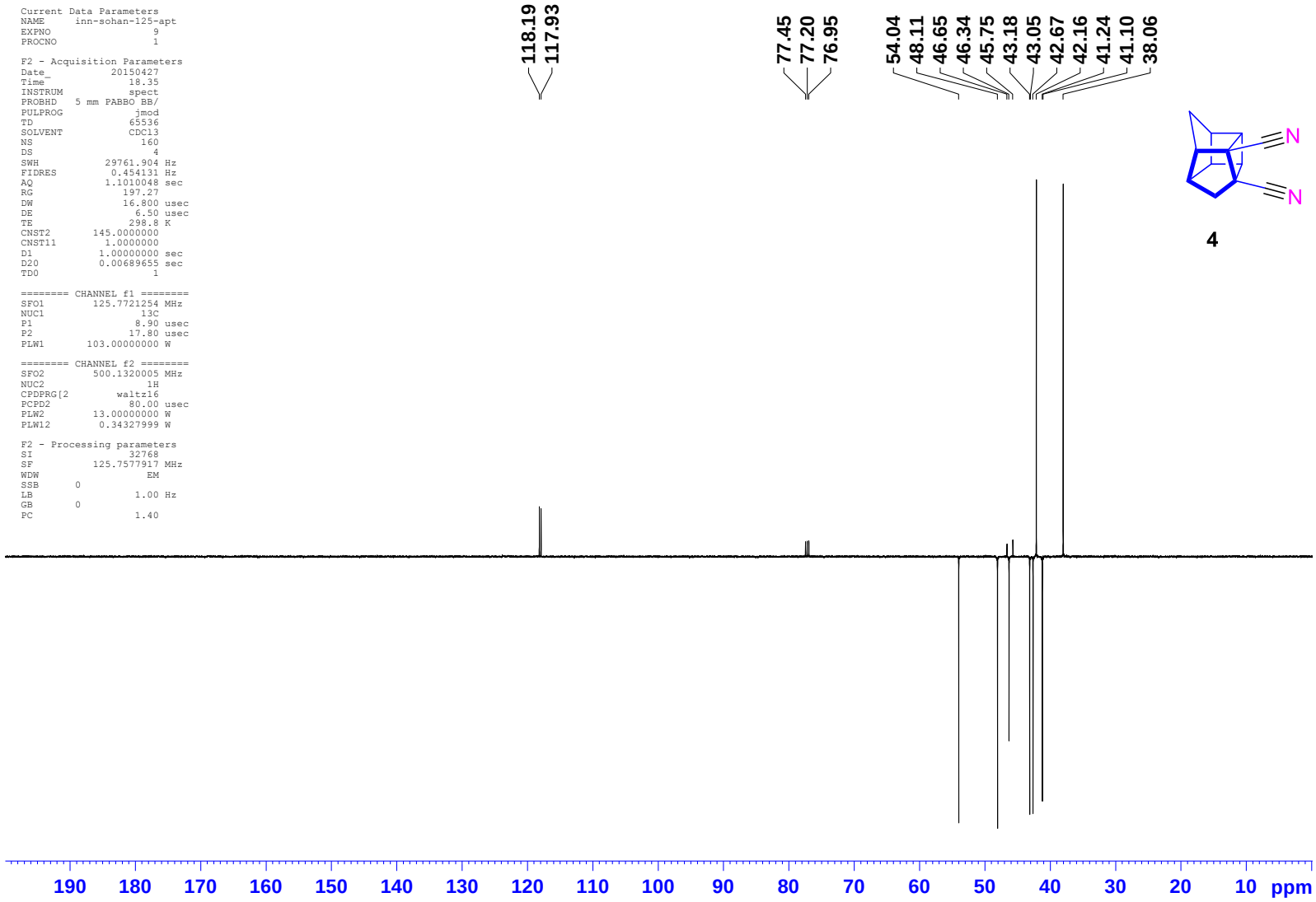


Fig. S10.^{13}C-APT NMR Spectrum of DCBHC 4

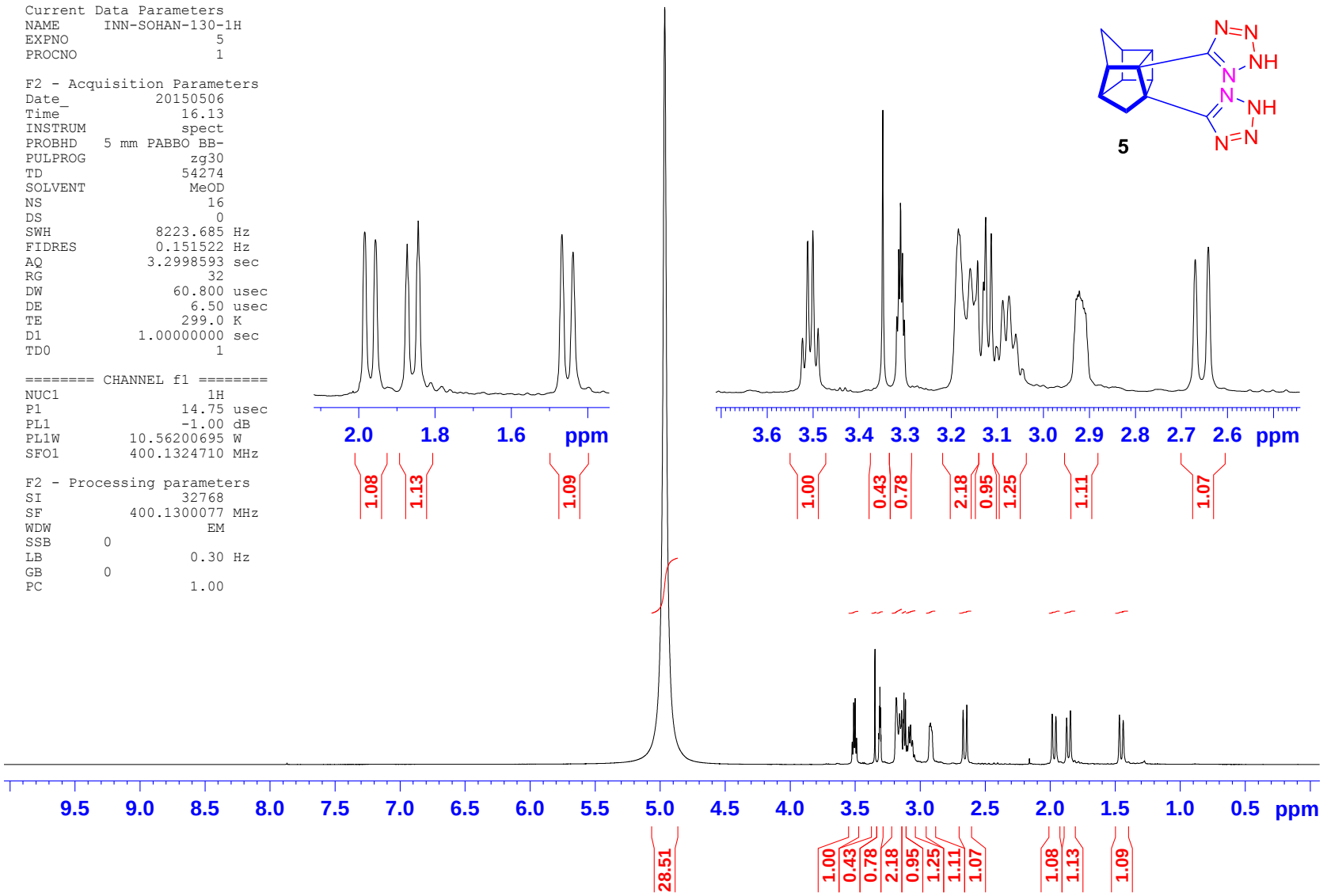


Fig. S11.^{1}H NMR Spectrum of DTetzBHC 5

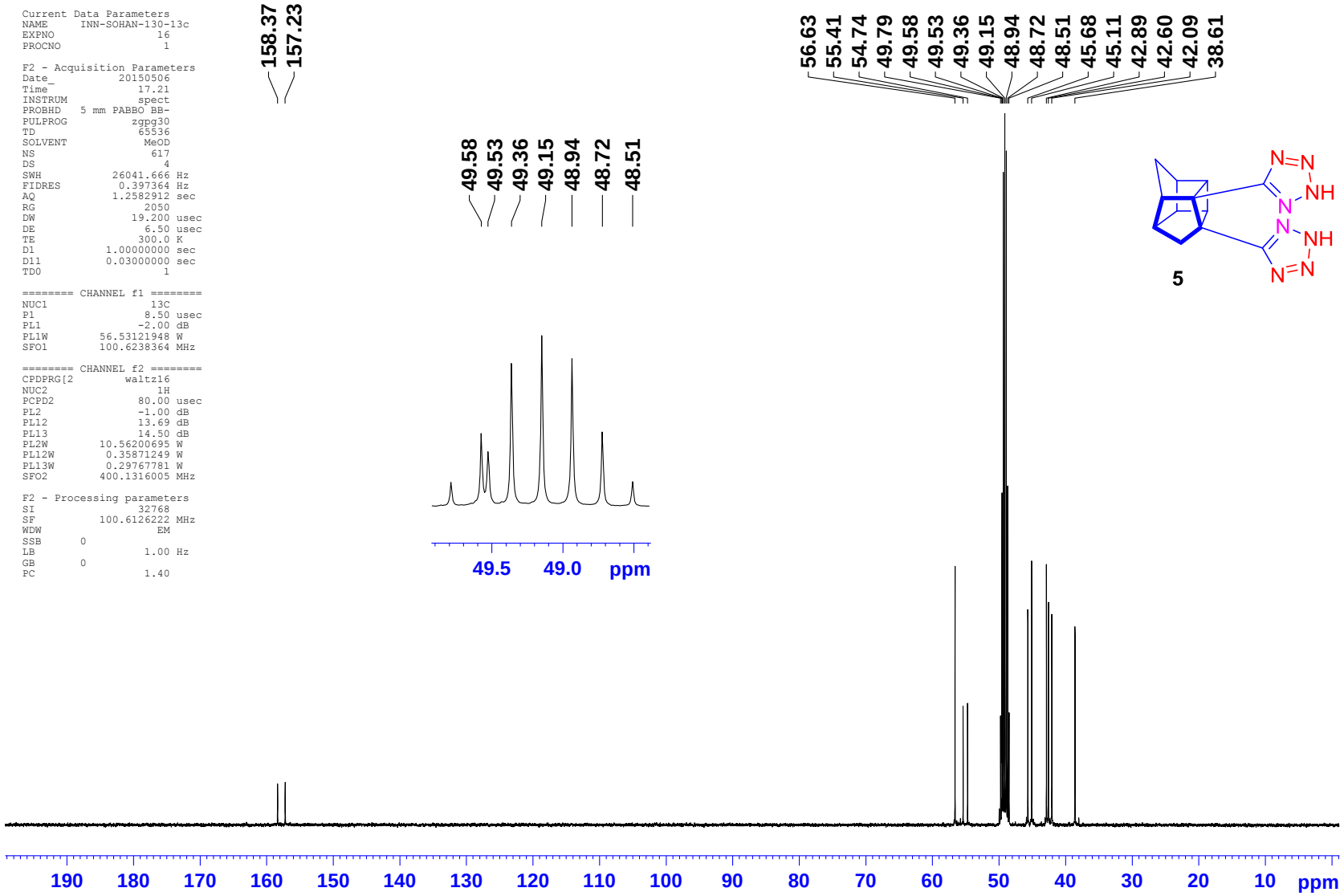


Fig. S12.^{13}C NMR Spectrum of DTetzBHC 5

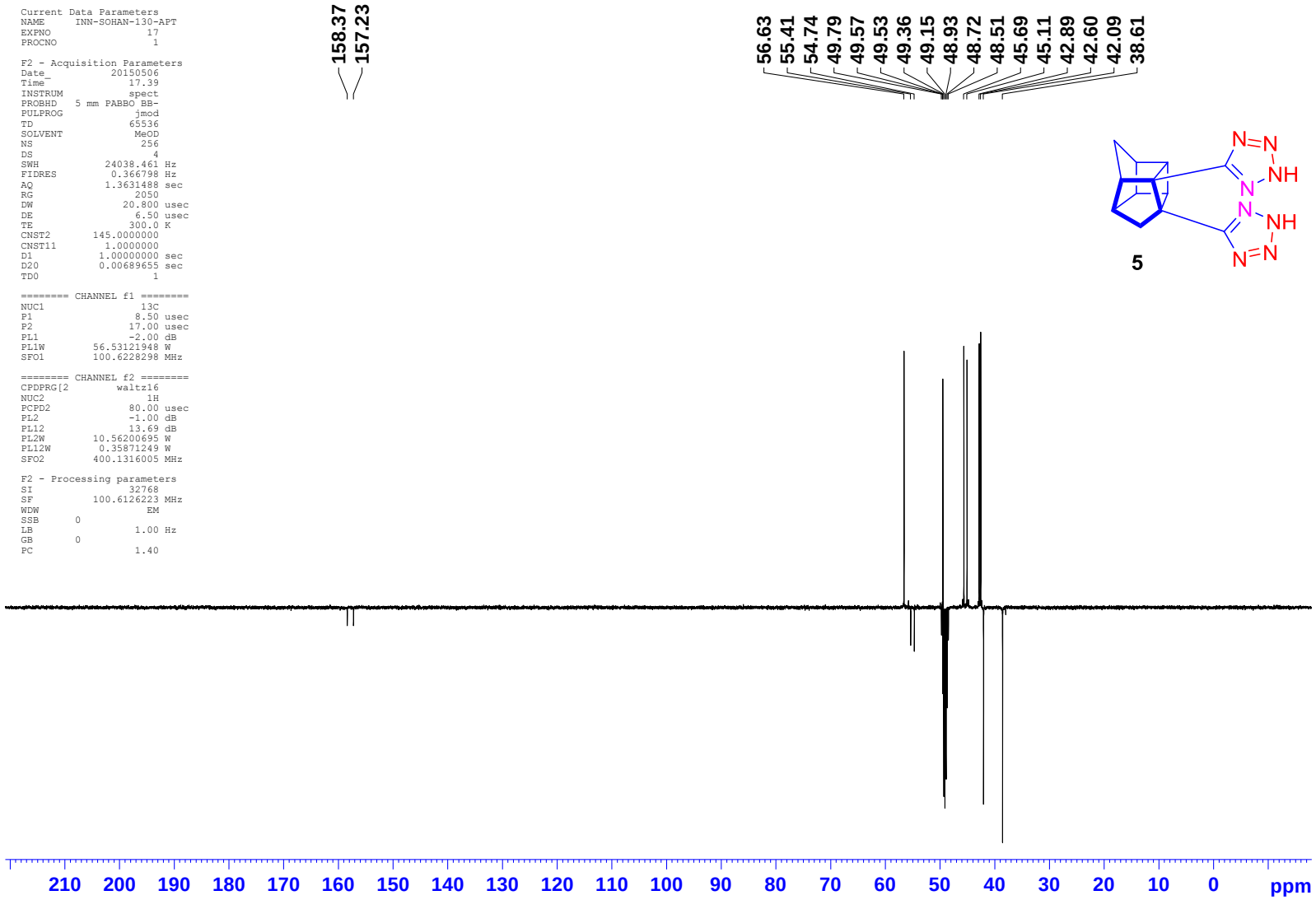


Fig. S13.^{13}C-APT NMR Spectrum of DTetzBHC 5